HEAT STERILIZABLE Ni-Cd BATTERY DEVELOPMENT

Jet Propulsion Laboratory
Contract No. 951972, Modification No. 3

Report for Sixth Quarter
October 1 to December 31, 1968

TEXAS INSTRUMENTS
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by

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ABSTRACT

The objective of this work is the development of heat-sterilizable, hermetically sealed Ni-Cd cells for space applications.

The electrochemical characterization of the sterilized 17-plate factorial design cells is continuing. Data up to and including cycle 91 is presented.

Of the eight cells out of sixteen of the 17-plate cells that have failed, all but one employs the 14019 polypropylene separator. Only four cells remain from which a full factorial design could be made. An analysis of variance of the calculated factor effects has shown that concentration and amount of electrolyte do affect the electrochemical characteristics, but that the significance of their effect is difficult to estimate because of the small number of cells involved.

Both core compression and separator wettability were investigated as possible causes for the lack of reproducibility of cycling data. Although core compression does have an effect on reproducibility, it appears that separator wettability is the most significant factor involved. The set of 18-plate cells constructed in September continues to perform well with much less scatter in the data. Cell-to-cell uniformity is excellent, and discharge behavior is uniform from cell to cell and cycle to cycle. The high end of charge voltage remains in evidence.

Wettability studies have shown that the separator having the best absorption characteristics are also those that do not stand up under the sterilization process (e.g. Pellon (nylon) and 14019 polypropylene). Treatments to improve the wettability of the FT2140 material include oxidative treatment, addition of surfactants to the electrolyte and proprietary treatments. Of these the first does not appear to be effective, while the second two are only moderately effective. Cells were constructed with 3M Company FC-128 and FC-176 surfactants in the electrolyte and are being tested presently.

The high end-of-charge voltage is being investigated. An experiment to test the effect of sterilization on components both alone and in certain combinations was carried out, and has shown that both electrodes undergo color changes when sterilized in the presence of KOH and separator.

The impact testing facility set up at Brown University is described.

1.0 INTRODUCTION

This is the sixth quarterly progress report on the heat-sterilizable nickel-cadmium battery development under Jet Propulsion Laboratory Contract No. 951972, Modification No. 3, sponsored under NASA Contract NAS-7-100, Task Order No. RD-26. The object of this contract is to perform research and development work leading to the design, development, fabrication and testing of sealed, rechargeable, nickel-cadmium cells capable of heat-sterilization.

The heat sterilization requirements include testing at 135°C for type approval and at 125°C for flight acceptance. At the 135°C sterilization temperature, the heating rate is 19°C/hour. The chamber is cooled at the same rate at which it is heated. Two such cycles are required. For preliminary testing, one 120-hour cycle may be used.

Since the fourth quarterly report, five new specific tasks have been added to the original contract. Essentially, however, these several tasks may be incorporated into one of four broad categories: 1) Electrochemistry, involving statistical and other experiments aimed at characterizing and optimizing electrodes, electrolyte and separators for heat-sterilizable Ni-Cd cells, 2) Case and Seal Design, for hermetically sealed, rechargeable, heat-sterilizable cells, 3) Fabrication - Performance - Cycle Life Testing necessary for the evaluation of 4 AH sealed, rectangular cells before and after sterilization, 4) Impact Testing of Cells, to evaluate the effects of high G-levels on cell performance and construction.

The emphasis now is to study and interpret the characteristic electrochemical behavior of sterilized cells, with a view of

optimizing cell design and thereby achieving cell to cell uniformity and reproducibility. The work performed during the sixth quarter is reported herein. Due to the resignation of Dr. J. P. Elder, Dr. R. W. Sorensen has been assigned to the project in the interim and will assume certain of Dr. Elder's responsibilities.

2.0 Electrochemical Investigations.

2.1 Ni-Cd Cell 2^n Factorial Experiment.

The factorial experiment was designed to discover effects of various factors on the behavior of heat sterilizable, hermetically sealed rechargeable Ni-Cd cells. The history of the cycled cells to date (12/31/68) is summarized in Figure I. Only half of the original 32 cells devoted to the factorial experiment are represented in Figure I since only these cells are being cycled presently. Of the cells not being cycled, one group of eight (cells numbered 4, 8, 12, 16, 20, 24, 28, 32) were cycled twenty-four times, sterilized, and set aside. The other groups of eight (cells numbered 2, 6, 10, 14, 18, 22, 26, 30) were cycled thirty-seven times and set aside without having been sterilized.

It is immediately apparent from Figure I that of the eight cells started with separator 14019, (Factor A, low level (0)), only one cell #13 in group I remains active. Three of the cells (no's. 3, 5, and 7) were opened and examined for the cause of failure. In cells #3 and #5, a short occurred between the negative electrode and the can, apparently because the outer layer of the separator had slipped upward slightly when the pack was inserted during cell assembly. There was indication of a short in the middle of the pack in cell #7. It is clear that sterilization weakens the 14019 separator in such a way that shorting becomes highly probable.

2.2 Cycling Studies on Selected Cells from Factorial Design.

The data presented in Figures 2 through 13 is a continuation of data presented in Figures 1 through 12 of the 5th quarterly report. Cycles through 30 were reported there, while in the present report, cycles 30 through 91 are reported. Data is presented on the following cells:

Cell	KOH (w/o)	Pore Fill (%)	Pressure Gauge Attach.	Capy. Fig. #	ECV Fig. #	ECR Fig. #
19	30	70	no	2	6	10
23	30	80	no	4	8	12
25	34	70	yes	3	7	11
31	34	80	no	5	9	13

It is interesting to compare the data of Figures 2 - 13 with the cycling history shown in Figure I. For example, a dramatic decrease in the average value of the end-of-charge voltage is evident at cycle 63 on all four cells. This corresponds to the change in charge routine noted in Figure I. Little change in the cell data occurred as a result of the removal of the pressure gauges from all cells but cell 13 at cycle 75.

There is very little that can be said in general about the delivered capacity on continued cycling. The high capacity noted in the previous report is maintained, and no decreasing trend is evident.

The decrease in end-of-charge voltage at cycle 63 brings the average level of end-of-charge voltage from 1.53v to about 1.46v. This latter value is nearly identical to the average end-of-charge voltage of cells taken after sterilization in Table 5 of the fifth quarterly report. This data had been obtained from cycles 3 and 6, which it will be recalled, were charged according to the same

charge routine (c/12.5 for 17 hours) as that used after cycle 63. Thus, the end of charge voltage behavior can be summed up as follows:

1) The increase observed after sterilization is highly dependent upon charge rate, increasing by approximately 50 mv for a two-fold increase in charge rate (c/10 to c/5).

2) The high post-sterilization end-of-charge voltage remains constant with continued cycling, as does its dependancy upon charge rate.

The end-of-charge resistances of cells 19 and 31 continue to be erratic, while this parameter is much more steady in cells 25 and 23. The amount of scatter in the data does not appear to correlate with any of the factors present in the experiment and is apparently due to some uncontrolled variable in the cell design.

2.3 Statistical Analysis of Data for Significant Effects:
An attempt was made to analyze the cycle data to see if electrolyte concentration and/or pore fill had any significant effect upon cell performance. Some difficulty was encountered in selecting cells for a suitable factorial analysis. Two of the original factors - type of separator and sterilization - are no longer valid. All but one of the cells employing the 14019 separator have failed. Only 37 cycles were carried out prior to sterilization so there are no pre-sterilization cycles to compare with cycles 37 through 91.

In order to employ as many cells as possible, a factorial experiment was designed with a full compliment of cells from group 1 of Figure 1, and nearly a full compliment from group 2. By "full compliment" is meant a total of four cells with all possible combinations of fill level and electrolyte concentration. For group 1, full compliment would be cells 17, 21, 25 and 29. For group 2, the corresponding cells would be 19, 23, 27 and 31 except

that cell 27 is missing. Therefore, the data for the corresponding cell of group 1 (cell 25) was substituted in order to make the calculation possible. Cells of group 1 had pressure gauges attached until cycle 75. Cells of group 2 did not. Thus, substitution of cell 25 for cell 27 in this experiment would tend to reduce the effects observed for presence or absence of pressure gauges.

The factors included are shown in Table I, Factors D and E were included so that data from several cycles could be averaged. These factors would be expected to have no effect other than to improve the statistical reliability of the data.

Factor C is shown in Table I as "pressure gauge treatment". However, it should be noted that all data were chosen from cycles after cycle 75 when the pressure gauges were removed. Thus, any significant effects observed for factor C would appear to be either permanent effects caused by the presence of a pressure gauge during early cycling, or some unknown difference in construction between the cells (i.e. "error").

TABLE I

Ni-Cd Rectangular 17-Plate Cell

Modified Factorial Experiment

Factor Designation	Description	LEVEL Low (0)	High (1)
A	% Pore Fill	70%	80%
B	Conc. KOH	30%	34%
C	Pres. Gauge Attach.	yes	no
D	Successive Cycles	n	n + 1
E	Cycle Number	n = 86	n = 90

The original data used for the statistical computations is given in Table II-A. The results of the analysis are summarized in Tables II-B and II-C. Very little significance could be attributed to the cycle factors, and, therefore, these effects and their consequent interactions are not shown. Therefore, the data given in the efficiency column of Table II-B and the ECV column of Table II-C is actually an average of the values given for four different cycles in Table II-A. The effects, variance ratios and significance values, however, are based upon all of the results shown in Table II-A, and not upon the average values.

The apparent results in Table II can be summarized as follows:

1. Cell efficiencies:
   A. There is a highly significant increase of 8.9% in the efficiency in going from 70 to 80% pore fill.
   B. There is a significant increase of 3.5% in the efficiency in going from 30 to 34% KOH.
   C. The increase in efficiency due to pore fill is less marked at higher electrolyte concentration than it is at the lower electrolyte concentration.
   D. Cells which did not have pressure gauges attached showed significantly greater efficiencies than cells that did have pressure gauges. This is noteable because the data was taken from cycles after the gauges had been removed. This effect, noted in previous reports while the gauges were still attached has apparently persisted for 10 to 15 cycles beyond the removal of the gauges.
2. End of charge voltages:
   A. Little significance is seen for increases or decreases in voltages due to either pore fill or electrolyte concentration.
   B. A significant increase in end of charge voltage results

TABLE II - A

Calculation and Significance Testing of Factor Effects

Ni-Cd, Rectangular, 17-Plate Cells, Theoretical Capacity: 4.96 AH

Cell/Cycle		A	B	C	D	E	Effc.	E.C.V.
17	86	0	0	0	0	0	.669	1.446
21	86	1	0	0	0	0	.746	1.450
25	86	0	1	0	0	0	.736	1.445
29	86	1	1	0	0	0	.766	1.445
19	86	0	0	1	0	0	.699	1.455
23	86	1	0	1	0	0	.820	1.447
25	86	0	1	1	0	0	.736	1.445
31	86	1	1	1	0	0	.830	1.447
17	87	0	0	0	1	0	.625	1.449
21	87	1	0	0	1	0	.712	1.451
25	87	0	1	0	1	0	.716	1.455
29	87	1	1	0	1	0	.750	1.448
19	87	0	0	1	1	0	.679	1.463
23	87	1	0	1	1	0	.813	1.458
25	87	0	1	1	1	0	.716	1.455
31	87	1	1	1	1	0	.823	1.460

Cell/Cycle		A	B	C	D	E	Effcy.	E.C.V.
17	90	0	0	0	0	1	.672	1.442
21	90	1	0	0	0	1	.739	1.448
25	90	0	1	0	0	1	.723	1.442
29	90	1	1	0	0	1	.759	1.442
19	90	0	0	1	0	1	.638	1.472
23	90	1	0	1	0	1	.800	1.467
25	90	0	1	1	0	1	.723	1.442
31	90	1	1	1	0	1	.810	1.477
17	91	0	0	0	1	1	.658	1.443
21	91	1	0	0	1	1	.750	1.447
25	91	0	1	0	1	1	.719	1.441
29	91	1	1	0	1	1	.763	1.440
19	91	0	0	1	1	1	.709	1.451
23	91	1	0	1	1	1	.840	1.458
25	91	0	1	1	1	1	.719	1.441
31	91	1	1	1	1	1	.844	1.459

TABLE II - B

Calculation and Significance Testing of Factor Effects

Ni-Cd, Rectangular, 17-Plate Cells. Theoretical Cap.: 4.96 AH

EFFICIENCY DATA

Cell	Factor Code A	B	C	Effcy.	Effect.	Variance Ratio	F-Test Significance	Significant Effects Primary	Interaction
17	0	0	0	.656					
21	1	0	0	.739	+.089	515.4	0.999999	A	
25	0	1	0	.723	.035	80.4	0.9999	B	
29	1	1	0	.759	-.020	24.9	0.997		AB
19	0	0	1	.681	.043	122.4	0.99997	C	
23	1	0	1	.818	.031	61.7	0.9998		AC
25	0	1	1	.723	-.010	6.3	0.9542		BC
31	1	1	1	.828	.003	0.0	0.0		ABC

TABLE II - C

Calculation and Significance Testing of Factor Effects

Ni-Cd, Rectangular, 17-Plate Cells. Theoretical Cap.: 4.96 AH

END OF CHARGE VOLTAGE DATA

Cell	Factor Code A	B	C	ECV (volts)	Effect.	Variance Ratio	F-Test Significance	Significant Effects Primary	Interaction
17	0	0	0	1.445					
21	1	0	0	1.449	0.0036	5.04	0.934	A	
25	0	1	0	1.446	-0.0039	6.15	0.952	B	
29	1	1	0	1.444	0.0029	3.42	0.886		AB
19	0	0	1	1.460	0.0102	41.2	0.9993	C	
23	1	0	1	1.457	0.0026	2.61	0.842		AC
25	0	1	1	1.446	-0.0017	1.13	0.671		BC
31	1	1	1	1.461	0.0059	14.00	0.990		ABC

from the absence of a pressure gauge. That is, cells without pressure gauges have an end-of-charge voltage that is on the average 10 mv. higher than cells with gauges.

C. The apparent interaction for all three variables is not based upon enough data to be considered a reliable effect.

The conclusions arrived at above are based upon the assumption that only the listed variables (% pore fill, KOH concentration, and pressure gauge attachment) are affecting the results. However, other experiments have shown that some less controllable variables such as pack compression and separator wettability can also affect cell behavior. If a large number of cells are used in factorial experiment of this nature such uncontrolled variables will show up as random error. The above conclusions are based on only 7 cells, and therefore, must be accepted with some caution since there is some likelihood that random errors, especially large ones, will not cancel with so few cells.

3.0 Studies of Factors Affecting Electrolyte Distribution:

The cycling history and data from the factorial experiments has raised a number of questions pertaining to the effect of sterilization on prismatic cells. First, what is the cause of significant increases in both cell capacity and end-of-charge voltages after sterilization? Second, why does the scatter of cell data decrease after sterilization? Third, the scatter of the data itself indicates that some parameter in the cell design remains uncontrolled. What is this parameter?

The third of these questions is important since scatter of the data could obscure more subtle phenomena resulting from sterilization. A very likely cause of the irreproducibility could be uneven electrolyte distribution, or insufficient wetting throughout the separator. Possible factors that control the electrolyte distribution such as core compression and separator wettability have, therefore, been investigated.

3.1 Ni-Cd Cell and Component Compression Studies:

In the Fifth Quarterly Report it was shown that 18 plate cells (8 positive, 10 negative) provided a core thickness that most readily matched the inner dimension of the case of the rectangular cells. It was felt that cells with 17 plates could be too loosely packed to provide suitably intimate contact with the electrodes for complete utilization of active material. The 19 plate cells required so much compression on the other hand, that permanent mechanical damage to components could result.

Three groups of 18 plate cells were assembled:

Group A: 5 charge-discharge cycles (at c/12.5 charge rate); 17 hours.

Group B: 5-charge-discharge cycles (c/12.5 charge rate); sterilized; continued cycling (c/12.5 charge rate).

Group C: Sterilized and cycled (c/12.5 charge rate).

Data for the five cycles prior to, and the first five cycles following sterilization were reported in the fifth Quarterly Report. In Table III is shown post-sterilization data for cycles on groups B and C run to date. In all, 30 cycles have been completed. Several remarks can be made:

1) Cell to cell and cycle to cycle uniformity is excellent. The difference between this result and the lack of uniformity in the 17-plate cells is remarkable.

2) As with 17-plate cells, the high end of charge voltage is always in evidence, further confirming the profound effect that sterilization has upon the electrochemical properties of the cells.

3) The efficiency of the 18-plate cells is, on the average,

TABLE III

Ni-Cd, Rectangular, 18-Plate Cells, 30% KOH, 80% Pore Fill

FT2140 Separator, Post-Sterilization Data

C.R. = c/12.5 C.L. = 137% D.R. = c/2.5

Cycle #	E.C.V. (V)		O.C.V. (V)		Cell Voltage at Various D. of D. 25%		50%		75%		E.C.R. (mΩ)		E.D.R. (mΩ)		CAP (A.H.)		EFF. (%)	
	Av.	σ	Av.	σ	Av.	σ	Av.	σ	Av.	σ	Av.	σ	Av.	σ	Av.	σ	Av.	σ
6	1.477	0.002	1.411	0.002	1.260	0.003	1.258	0.004	1.249	0.005	12.43	1.51	11.74	1.99	4.292	0.069	85.6	1.4
9	1.470	0.005	1.399	0.004	1.267	0.004	1.264	0.004	1.239	0.004	11.51	1.54	11.07	2.12	4.059	0.100	81.8	2.0
15	1.462	0.002	1.418	0.002	1.268	0.006	1.263	0.006	1.249	0.006	12.35	2.43	12.42	2.45	4.134	0.049	83.3	1.0
20	1.475	0.005	1.416	0.006	1.269	0.008	1.262	0.008	1.250	0.008	12.02	2.82	14.63	6.77	4.126	0.079	83.2	1.6
26	1.462	0.002	1.405	0.002	1.268	0.011	1.260	0.011	1.243	0.011	9.90	3.41	15.94	6.57	4.050	0.110	81.7	2.2
29	1.456	0.001	1.395	0.003	1.271	0.010	1.264	0.011	1.246	0.010	14.30	4.34	15.55	6.45	3.971	0.074	80.1	1.5

about 83% as compared to 69% for the 17-plate cells after sterilization and shows far more reproducibility.

4) Continued cycling produces greater cell to cell scatter of cell resistance data. Even still, a general tendency of cell resistance to increase is evident.

The cycling studies with the 18-plate cells are being continued.

The differences between 17-plate cells and 18-plate cells noted above indicate that core compression is a significant factor. An experiment was designed to assess this parameter more directly. Twenty-four 17-plate cells were prepared with 304 stainless steel shims in thicknesses of .010" and .020" placed as symmetrically as possible on the outside of the cell packs. A 17-plate cell pack with a .033" shim would be expected to be equivalent in thickness to an 18-plate cell. The shim thickness and the resulting cell performance is shown in Table IV.

TABLE IV

Core Compression Study

17-Plate Cell with FT2140 Separator, Cycle No. 3

Charge-Discharge Routine: Input: 1.00 amp, 5 hrs.
Output: 2.00 amps to 1v. cut-off

Pre-Sterilization

Shim Inches	ECV Volts	ECP* P.S.I.A.	ECR ohms	ECP* P.S.I.A.	EDR ohms	ECC A.H.	Force to Flatten (lbs.)
0.00	1.456	79.7	11.20	26.7	11.14	3.518	5.4
0.10	1.468	57.7	10.09	23.7	10.24	3.472	5.1
0.20	1.460	75.7	10.10	39.7	10.62	3.539	6.2
0.30	1.458	62.7	10.45	32.7	11.28	3.583	4.7
0.40	1.456	80.7	9.11	43.2	9.87	3.463	6.4
0.50	1.458	62.7	10.02	29.7	10.84	3.571	7.2

* Value for 1 cell - all other data average of 4 cells.

When prismatic cells are constructed, the walls of the case tend to bulge outward. When cycled, however, the cells are fixed between heavy, flat restraining plates. This would tend to place more compression on the thicker packs than on the thin packs. However, no correlation is evident between the shim thickness and the force to flatten, even though it was determined that the force to flatten empty cells filled with air at a known pressure was proportional to this pressure.

The very poor correlation among the cell parameters and the shim thicknesses or the force to flatten seems to preclude the conclusion that cell compression is an important variable.

However, it should be noted that even the well behaved 18-plate cells showed low efficiencies and poor reproducibility prior to sterilization. In fact, both groups showed pre-sterilization efficiencies of 60%. The most notable differences between 17-plate and 18-plate cells occurred after sterilization. Unfortunately, follow-up studies on sterilized shim cells have not yet been carried out so any conclusion as to the effect of core compression, on cell behavior must be deferred for the present.

3.2 Separator-Electrolyte Wettability Studies:

The lack of reproducibility of cell data may result from poor absorption of electrolyte by the polypropylene separator materials. Poor wetting of the separator would be influenced by pressure on the plates, thereby accounting for the differences observed between 17 and 18 plate cells. The net result of poor wetting properties could be an uneven and irreproducible distribution of electrolyte which in turn would cause uneven utilization of the active electrode material.

Experiments to test the wetting properties of separator materials

were performed as follows: a 1 cm x 25 cm strip of the material under investigation was suspended in a 100 ml graduated cylinder. The lower end of the strip was immersed just below the surface of a reservoir of a 30% potassium hydroxide solution. The distance between the surface of KOH reservoir and the point on the strip to which the electrolyte had risen was measured as a function of time. Since data extended over several orders of magnitude, it is presented as a log-log plot in Figure 14.

It is immediately apparent from Figure 14 that all of the as-received untreated polypropylene separators show lower rates of absorption than the nylon (Pellon) separator material. Also, the wetting properties of the FT2140 separator are poorer than unsterilized 14019 whether the FT2140 has been sterilized or not. Even though sterilization improves the wetting properties of the FT2140 separator, they are so poor in comparison with nylon that the poor observed performance of the cells is understandable on the basis of this factor alone. Since, however, the FT2140 separator has shown an ability to stand up under sterilization (while nylon and the 14019 polypropylene have not) attempts were made to enhance the wetting properties of the FT2140 material.

Three approaches to the improvement of the FT2140 wetting properties were considered:

1) Oxidative Surface Treatment of the Separator Material
2) Modification of the Wetting Properties of the Electrolyte by Surfactant Addition
3) Use of Proprietary Treatments on the Separator Material

3.2.1. Oxidative Surface Treatment:

Chromic acid oxidative treatments have been employed to modify the hydrophillic character of the surface and to control the wettability of polyethylene films. Acetic/sulphuric acid solutions of dichromate have been shown to effect oxidations of saturated hydrocarbons.

The wetting properties of type FT2140 separator, however, were found to be unaffected significantly by oxidative surface treatments. This was shown by the results of the following experiments:

Four solutions were prepared, each consisting of a solution of 10 ml 2N sodium dichromate/10 ml concentrated sulphuric acid, added to 90 ml of A, deionized water; B, acetone; C, acetic acid; D, concentrated sulphuric acid. Solution B was quickly eliminated because of oxidation of the acetone. Samples of as-received FT2140 material were immersed at room temperature for varying periods of time. Following immersion, the samples were reached in deionized water for 1 1/4 hrs. and then dried at 70°C for 1 1/2 hrs. Absorption rate studies were then performed on the several treated samples.

The results of the absorption studies are listed in Table V.

TABLE V

Comparison of Wetting Properties of FT2140 Separator with 30% KOH after Various Treatments

Treatment	Immersion Time (minutes)	Time (min.) to Reach Height of: 0.5 cm	1.0 cm	2.5 cm
None	--	200	400	> 400
Sterilization	--	20	44	> 44
Sol. A	30	1500	>1500	> 1500
Sol. A	60	130	150	200
Sol. A'	90	800	1500	> 1500
Sol. A	120	1700	>1700	> 1700
Sol. C	60	110	160	400
Sol. D	60	290	400	> 400

The times required for the 30% potassium hydroxide to rise to a height of 0.5, 1.0 and 2.0 cm in the separator above the reservoir level are given. After 60 min. immersion, the treatments with the aqueous and acetic acid solutions A and C have comparable effects. Treatment with the concentrated chromic acid, solution D, has no beneficial effect. With solution A, an optimum immersion time of approximately 60 min. is indicated. However, in comparison with the effects produced by sterilization, the enhancement of the absorption rate by chemical oxidation is not very significant.

3.2.2. Modification of Electrolyte by Surfactant Addition

Absorption studies were carried out with electrolyte solutions (30% KOH) containing various surfactants. The surfactants were chosen for their known ability to remain stable under electrochemical oxidizing or reducing conditions. The electrolyte solutions were prepared as follows:

Five cc of 0.1% surfactant solution were added to 50 cc of 34% KOH giving a resulting solution of 30 to 31% in KOH, and .01% in surfactant. The surfactants were:

Rohm & Haas Triton X-100
3M Company FC-98
" " FC-128
" " FC-170
" " FC-172
" " FC-176

Of these, only types FC-128 and FC-176 were efficient enough in enhancing the electrolyte wetting properties to warrant further investigation.

Therefore, a series of absorption studies using several concentrations of these two surfactants were performed on FT2140 separator.

The experiments were performed on the separator in the as-received condition and after an oxidative pre-treatment. The pre-treatment used was that described above-immersing for 60 min. in a dilute chromic acid solution (Solution A). As can be seen from Table VI, the FC-128 surfactant is most effective in enhancing the wettability properties of the FT2140 separator.

TABLE VI

Effect of Surfactants on Wetting Properties of As-Received and Pre-Treated FT2140 with 30% KOH

Surfactant	Concentration ppm	FT2140 Pre-Treat.	Time to Attain a Height of 0.5 cm (min.)	1.0 cm (min.)	1.5 cm (min.)
None	--	none	200	400	>400
FC-128	100	none	14	80	650
	100	Chromic Ac.	2	7	34
	200	none	16	45	200
	200	Chromic Ac.	1	5	21
	500	none	1	6	46
	500	Chromic Ac.	1	4	21
	saturated	none	1	4	45
	"	Chromic Ac.	1	3	21
FC-176	100	none	300	150	1500
	100	Chromic Ac.	100	>1000	>1000
	200	none	50	120	1000
	200	Chromic Ac.	40	130	600
	500	none	40	95	600
	500	Chromic Ac.	30	85	500
	1000	none	35	75	300
	1000	Chromic Ac.	2	80	500

Furthermore, the wettability increases with increasing concentration of the surfactant, and is ultimately limited only by the solubility of the surfactant in 37% KOH. The solubility limit is only slightly higher than 500 ppm. Again it can be seen that the oxidation treatment of the separator offers only a slight improvement of the wetting properties.

The effect of 500 ppm additions of the FC-128 and the FC-176 surfactants on cell operational behavior is being studied. Four groups of five 18-plate cells each were constructed:

Group (1) control - no surfactant no oxidative treatment of FT2140 separator

Group (2) chromic acid treatment - no surfactant

Group (3) 500 ppm FC-128 added - no chromic acid treatment.

Group (4) 500 ppm FC-176 added - no chromic acid treatment.

Results of cycling studies now in progress on these cells will be reported in the seventh quarterly report.

3.2.3. Proprietary Treatments on Separator Material

A series of electrolyte absorption studies have been performed on Gelman proprietary treated polypropylene. As can be seen in Figure 14 the absorption rate of this as-received material is only slightly less than that exhibited by nylon. However, after sterilization in 30% KOH, washing and drying, the wetting properties deteriorate considerably. Other experiments measuring the grams of liquid electrolyte retained by a given weight of separator (pick-up) showed that the weight retained by the unsterilized Gelman material was greater if withdrawn immediately after immersion in 30% KOH than if withdrawn after 64 hrs. This indicates a possible change in wetting properties, and/or an attack upon the material by the electrolyte. Table VII gives results of pick-up experiments for both FT2140 separator material, and for the Gelman material under various conditions. It is noteworthy that the FT2140 does not show an immediate pick-up, and that an extended immersion is required.

TABLE VII

Gelman and FT2140 Polypropylene

30% KOH Solution Pick-Up

Polypropylene Type	Conditions	Pick-Up (grams KOH/grams separator) Sample #1	Sample #2
FT2140	64 hr. immersion	3.69	3.20
Gelman	immediate	2.45	2.41
Gelman	64 hr. immersion	1.98	1.75
Gelman (sterilized)	immediate	2.69	----

Four 17-plate cells employing the Gelman separator were constructed, two with the separator nap facing the positive plate (P-1 and P-2) and two with the nap facing the negative plate (N-1 and N-2). The cells were cycled 10 cycles prior to and 16 cycles after sterilization. Data for cells P-2 and N-2 is shown in Table VIII. Prior to sterilization, cells P-1 and P-2 yielded slightly higher efficiencies than cells N-1 and N-2. After sterilization, the end-of-charge voltage was found to be increased. The efficiencies increased (6% for P-2 and 13% for N-2) over their pre-sterilization values. With continued post-sterilization cycling the E.C.V. decreased from highs of 1.512v for Cell P-2 and 1.507v for cell N-2 to average (cycles 7-16) of 1.467 and 1.463 respectively, but never attained the pre-sterilization levels of 1.437 and 1.439 respectively. The efficiency of cell P-2 did drop from a high of 71.6 on the first cycle after sterilization to the pre-sterilization level of 62.3% after 6 cycles. (The average efficiency for cell P-2 on post sterilization cycles, 7 through 16 was 62.6%). However, cell N-2 achieved a high of 71.2% after sterilization and dropped only to an average (cycles 7-16) of 63.5 as opposed to its pre-sterilization average (over 10 cycles) of 52.4%. These cells showed far less scatter than that previously observed in the cycled factorial design 17-plate cells. Post-sterilization

TABLE VIII

Cycle Data for Gelman Separator, 17-Plate Ni-Cd
Pre- and Post-Sterilized Cells

		CELL P-2					CELL N-2				
Condition	Cycle #	ECV (v)	ECR (mΩ)	EDR (mΩ)	CAP (AH)	EFFCY (%)	ECV (v)	ECR (mΩ)	EDR (mΩ)	CAP (AH)	EFFCY (%)
Pre-Ster.	1	1.440	10.42	11.10	2.652	53.5	1.433	10.58	10.78	2.552	51.5
"	2	1.429	10.64	11.11	2.918	58.8	1.430	11.21	10.50	2.584	52.1
"	3	1.438	10.79	10.78	3.066	61.8	1.438	11.06	10.11	2.634	53.1
"	4	1.432	10.42	10.60	2.918	58.8	1.435	10.38	9.86	2.466	49.7
"	5	1.434	10.76	11.06	3.100	62.5	1.434	10.87	10.45	2.684	54.1
"	6	1.440	10.28	11.15	3.484	70.2	1.442	10.20	10.47	2.952	59.5
"	7	1.437	10.37	10.68	3.252	65.6	1.440	10.22	10.16	2.818	56.8
"	8	1.434	10.80	10.30	3.118	62.9	1.441	10.72	9.77	2.734	55.1
"	9	1.442	10.66	10.53	3.200	64.5	1.447	10.47	9.84	2.852	57.5
"	10	1.445	10.62	10.63	3.218	64.9	1.449	10.40	10.00	2.866	57.8
Post-Ster.	1	1.512	9.12	9.86	3.552	71.6	1.507	9.32	10.06	3.534	71.2
"	2	1.482	8.47	9.54	3.500	70.6	1.479	8.72	9.71	3.484	70.2
"	3	1.474	10.25	11.11	3.334	67.2	1.471	10.59	11.28	3.366	67.9
"	4	1.464	20.50	10.72	3.134	63.2	1.459	10.55	10.98	3.200	64.5
"	5	1.493	9.78	11.00	3.166	63.8	1.483	10.00	10.92	3.166	63.8
"	6	1.466	7.07	10.89	3.084	62.2	1.462	7.25	11.14	3.118	62.9
"	7	1.469	10.15	10.74	3.066	61.8	1.465	10.39	10.85	3.100	62.5
"	8	1.464	9.99	11.30	2.966	59.8	1.461	10.23	11.50	3.018	60.8
"	9	1.462	10.04	10.42	3.066	61.8	1.458	10.15	10.55	3.084	62.2
"	10	1.489	10.12	10.83	3.166	63.8	1.481	10.22	10.92	3.200	64.5
"	11	1.457	10.25	10.85	3.118	62.9	1.453	10.32	11.01	3.166	63.8
"	12	1.454	10.11	11.23	3.134	63.2	1.452	10.24	11.21	3.184	64.2
"	13	1.464	9.73	10.95	3.166	63.8	1.461	9.97	10.98	3.200	64.5
"	14	1.470	10.47	10.27	3.084	62.2	1.466	10.37	10.38	3.152	63.5
"	15	1.473	10.08	10.83	3.184	64.2	1.469	10.21	10.86	3.218	64.9
"	16	1.473	11.21	10.26	3.100	62.5	1.469	9.78	10.46	3.166	63.8

cycling studies are being continued.

The differences observed between cells with separator nap facing positive or negative plate cells warranted further investigation. Therefore, a number of 17-plate and 18-plate cells with FT2140 separator were constructed such that the nap faced:

a) negative plates
b) positive plates
c) both negative and positive plates

The cells were cycled five times charging at the c/12.5 rate to 137% charge level and discharging at the c/2.5 rate to a 1v cut-off. Following these cycles, the cells were sterilized and cycling continued. The results do not show any marked differences between the various separator-electrode configurations, but the differences between before and after sterilization data, and 17-plate and 18-plate cells are significant.

A summary of data taken from the 5th cycles before and the 5th cycles after sterilization is given in Table IX. Each entry for a given configuration (e.g. nap facing neg., 17-plate, pre-sterilization) is an average for the three cells constructed with that configuration. The average values for all pre-sterilization 17-plate cells are therefore for a total of nine cells and all pre-sterilized cells total 18 cells. The post-sterilization values are for the same 18 cells after sterilization. The same trends that were noted previously are apparent here; that is ECV, OCV and efficiency all increase upon sterilization. It is also noteworthy that a very low efficiency of 42.5 occurs for 18-plate cells prior to sterilization and that the efficiency of these cells increases to the highest value after sterilization. Since no marked effect was observed to result from differences in separator nap configurations, however, this series of tests was terminated.

TABLE IX

Ni-Cd Rectangular Cells 30% KOH, 80% Pore Fill
FT2140 Separator. Data from 5th Cycle Before & 5th Cycle
After Sterilization. C.R.=c/12/5 C.L.=137% D.R.=c/2.5

Condition	ECV (volts)	OCV (volts)	Effcy. (%)
Nap Facing Neg., 17-Plate, Pre-sterilization	1.421	1.372	66.6
Nap Facing Pos., 17-Plate, Pre-sterilization	1.438	1.376	76.0
Nap Facing Both, 17-Plate, Pre-sterilization	1.425	1.372	61.1
Average of above, 17-Plate, Pre-sterilization	1.428	1.373	67.3
Nap Facing Neg., 18-Plate, Pre-sterilization	1.410	1.368	43.7
Nap Facing Pos., 18-Plate, Pre-sterilization	1.406	1.366	40.3
Nap Facing Both, 18-Plate, Pre-sterilization	1.412	1.369	43.5
Average of Above, 18-Plate, Pre-sterilization	1.409	1.368	42.5
Average of All, Pre-sterilization	1.418	1.371	54.9
Nap Facing Neg., 17-Plate, Post-sterilization	1.496	1.405	73.3
Nap Facing Pos., 17-Plate, Post-sterilization	1.488	1.403	64.6
Nap Facing Both, 17-Plate, Post-sterilization	1.498	1.406	72.6
Average of Above, 17-Plate, Post-sterilization	1.494	1.405	70.2
Nap Facing Neg., 18-Plate, Post-sterilization	1.489	1.411	77.4
Nap Facing Pos., 18-Plate, Post-sterilization	1.485	1.410	76.2
Nap Facing Both, 18-Plate, Post-sterilization	1.481	1.413	75.3
Average of Above, 18-Plate, Post-sterilization	1.485	1.411	76.3
Average of All, Post-sterilization	1.489	1.408	73.2

4.0 Preparation of Separately Sterilized Components:

Efforts were initiated in this quarter to determine the cause of the increase in the end-of-charge voltage and, the cell efficiencies. In order to evaluate the effects of sterilization on the components both separately and in combination, sterilization was carried out according to the following scheme where + indicates the presence of a particular component and 0 its absence:

ITEM	POSITIVE	NEGATIVE	SEPARATOR	ELECTROLYTE
1	+	0	0	0
2	0	+	0	0
3	0	0	+	0
4	+	0	0	+
5	0	+	0	+
6	0	0	+	+
7	+	0	+	+
8	0	+	+	+

The separator used was type FT2140 and the KOH concentration was 30%. Samples were sterilized for 64 hrs. at 135°C. Items 1-3 were heated in air while 4-8 were sealed in standard battery cans. After sterilization, items 4-8 were washed free of KOH, air dried at 100°C and stored in a dessicator.

The normally black positives became blue-grey when sterilized in the presence of KOH or KOH and separator. The blue-grey negatives became less blue and more grey under the same conditions. The separator became stiffer under all conditions and tore more readily after drying, particularly when it had been sterilized in the presence of electrolyte and positive.

5.0 Impact Testing Facility:

Following a study of the JPL slingshot machine used for high impact investigations, our work has been directed toward modification of similar equipment at Brown University. We have at our disposal a

pneumatic Hyge gun operating on high pressure nitrogen and rated at 40,000 pounds thrust. We have used a two-rail intermediate section approximately six feet long. Completing the system is a 2500 pound steel block mounted on rollers and shock absorbers to serve as the anvil mass. Thus main design emphasis was placed on the carriage assembly. It was desirable to strive for: (a) a single fixture arrangement compatible with every cell configuration we expect to evaluate: (b) minimize the effect of various cell weights on attained velocity, thus permitting a single calibration of the accelerating mechanism; (c) compromise with total weight to limit the amount of energy that must be dissipated; (d) not only survival of the specified 4000g-1 msec, but the capability to explore various g-levels for various pulse lengths.

The carriage and other mechanical components have been built and approximately 40 tests have been run for calibration and instrumentation setup. The total carriage weight is approximately 32.5 pounds and thus we have a higher amount of energy to dissipate at any given velocity. This can be seen in the brief representative values obtained to date. For the most part, larger tool diameters are required for a given g-level than found necessary by JPL.

Tool Diameter	Measured g-Level	Calculated g-Level
1/2"	1200	1100
5/8"	1800	1700
3/4"	2700	
7/8"	3400	3400
1"	4800	4200

These values are average and representative only. Additional calibration runs are required to finalize the values. We conducted test runs at velocities of 75-125 ft./sec. The pulse shape has been essentially square for durations from 1-2 msec. depending on velocities and tool diameters. An excellent correlation between

tool area and g-level has been indicated in the preliminary work. This is encouraging in the sense that work hardening or strain rate effects may be small, thus assuring the square pulse shape through various durations or deceleration time.

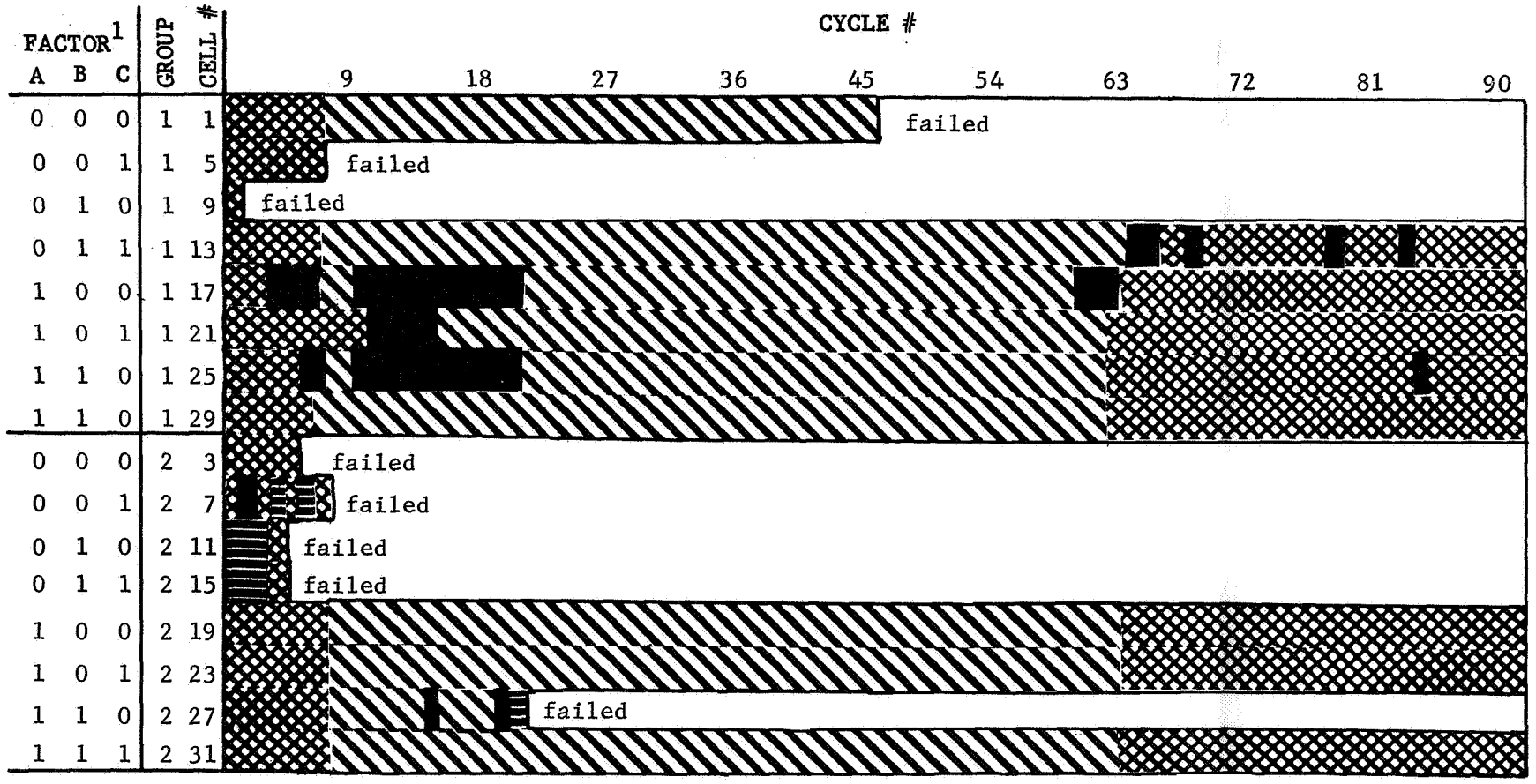
The measurement of impact velocity is achieved by two brittle wire contact points at known distance and an electronic time interval counter. This system has demonstrated excellent reliability. Time measurement in μ seconds implies an accuracy of 1% dictated by contact location variance. Likewise, we have demonstrated a technique to reliably record cell voltage during impact. We are experiencing some practical difficulties in reliably controlling the dynamic motion of the instrumentation cables during impact. A new counterspring system will be employed which should prove more permanent. Associated problems in acceleration measurement are being actively eliminated. Of prime concern are effects due to the elastic wave propagation within the carriage and the excitation of mounted accelerometer resonant frequency. During this critical time of testing facility development, we feel it is advantageous to spend time in gaining a full understanding of the apparatus. We are, therefore, conservative in employing simple solutions such as filter networks. We need an understanding of high frequency response in our particular system in order to reproduce precise waveforms and to achieve various types of pulse shapes in later dynamic investigations. Several approaches are under study to improve the data acquisition with a minimum of distortion.

Initial impact work will involve the programmed testing of existing Ni-Cd cells to identify failure modes and relative quantitative impact resistance. This initial phase will begin during January when instrumentation development and system calibration has been completed.

Fig. 1

Ni-Cd RECTANGULAR 17-PLATE CELLS, THEORETICAL CAPACITY (FORMATION) 4.96 AH

FACTORIAL EXPERIMENT. POST-STERILIZATION CYCLING HISTORY TO 12/31/68



Factor Code

Factor		Level Low(0)	Level High(1)
A	Separator	14019	FT2140
B	Conc. KOH	30%	34%
C	% Pore Fill	70%	80%

Group 1 - Cells with pressure gauges (until Cycle 75)

Group 2 - Cells without pressure gauges

BAR-GRAPH KEY

Charge at C/12.5 for 17 hrs to 137% level.

Discharge at C/2.5 to 1 V cut-off.

Charge at C/5 for 5 hrs to 100% level.

Discharge at C/2.5 to 1 V cut-off.

Not fully charged due to pressure cut-off.

Not fully charged due to shorting or other unknown cause.

Fig. 2

AMPERE CAPACITY OF 17 PLATE FACTORIAL CELLS VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR

30% KOH, 70% PORE FILL

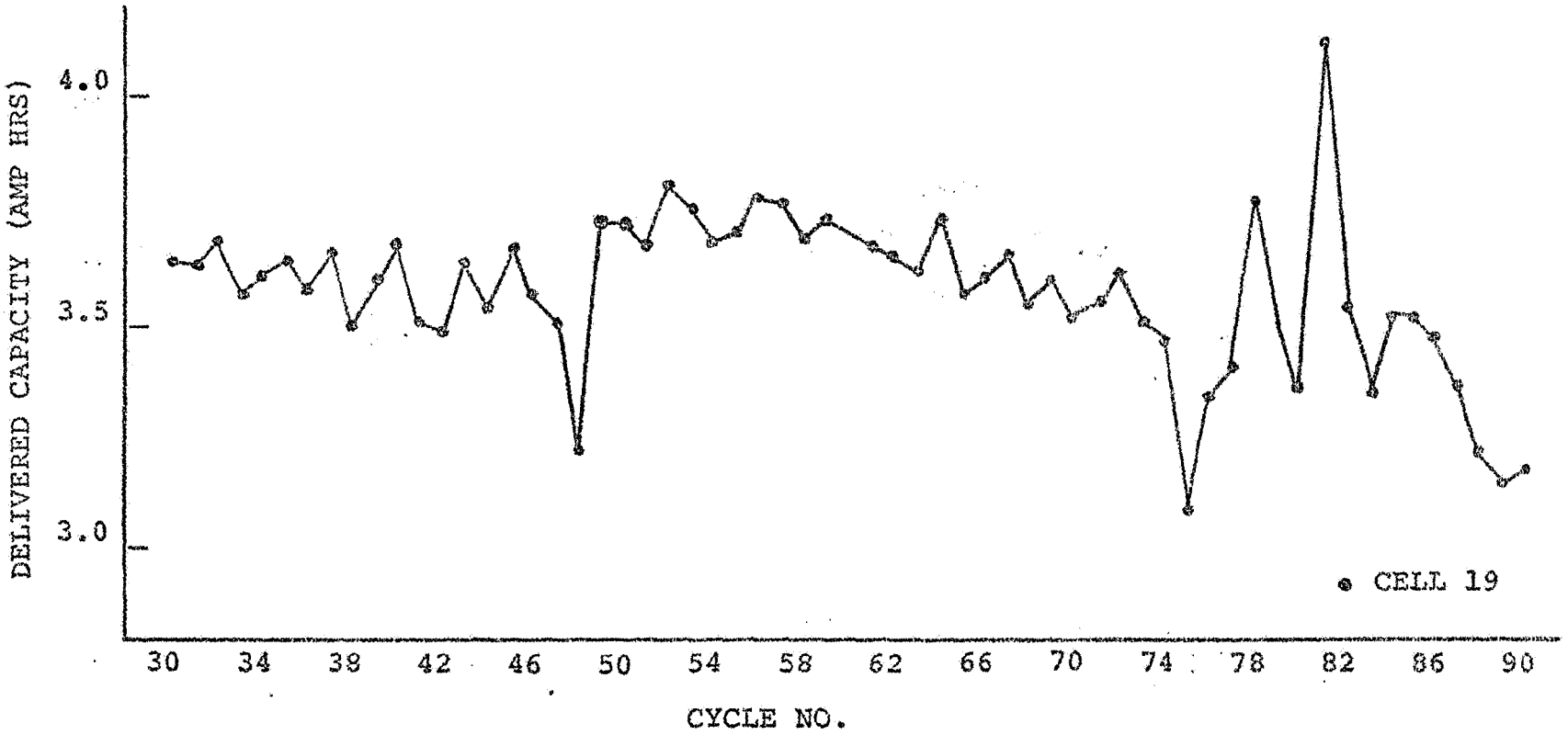


FIG. 3

AMPERE CAPACITY OF 17 PLATE FACTORIAL CELLS VS. CYCLE NUMBER
POST STERILIZATION
CELL DESIGN: TYPE FT2140 SEPARATOR
34% KOH, 70% PORE FILL

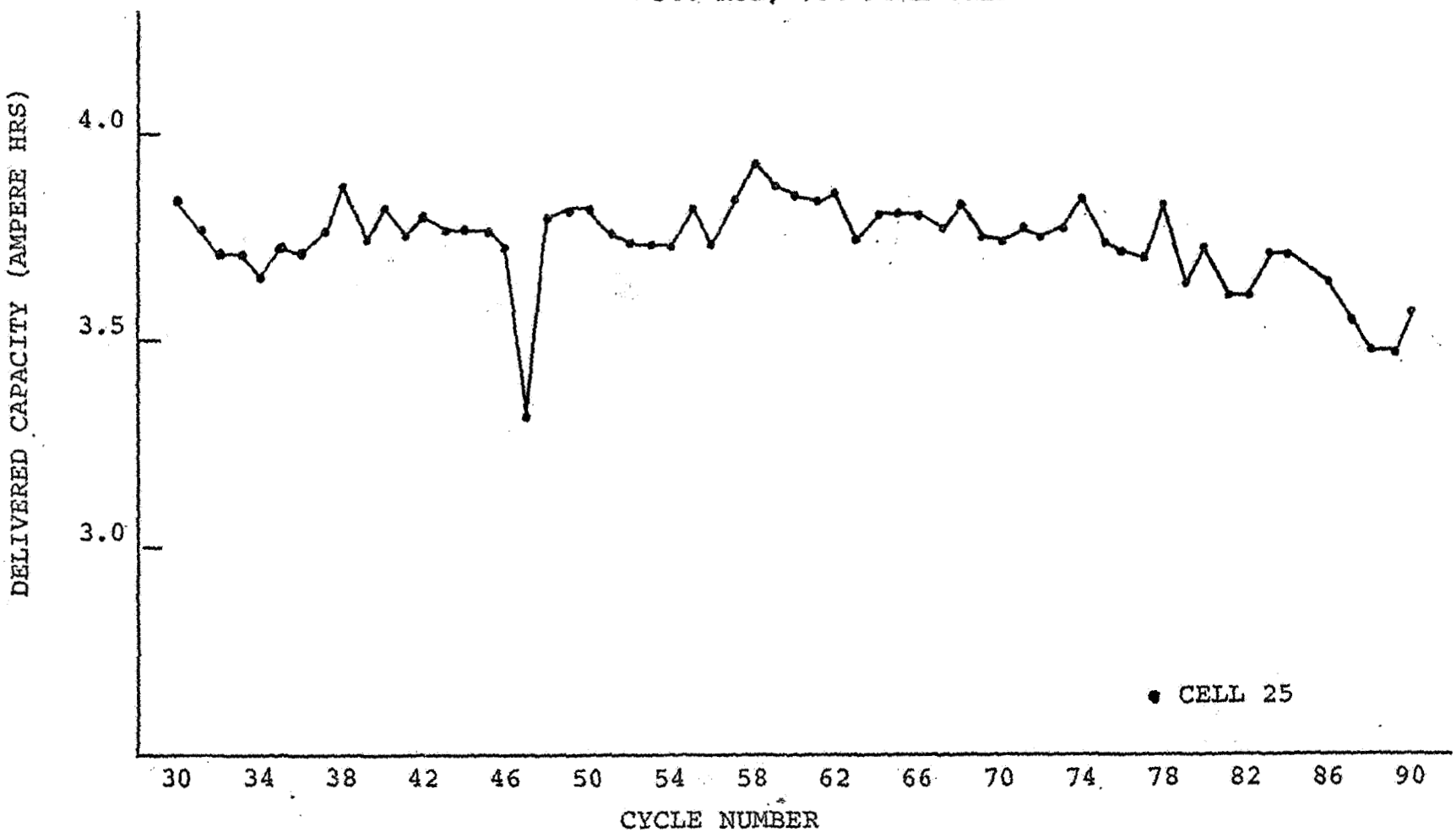


FIG. 4

AMPERE CAPACITY OF 17 PLATE FACTORIAL CELLS VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR

30% KOH, 80% PORE FILL

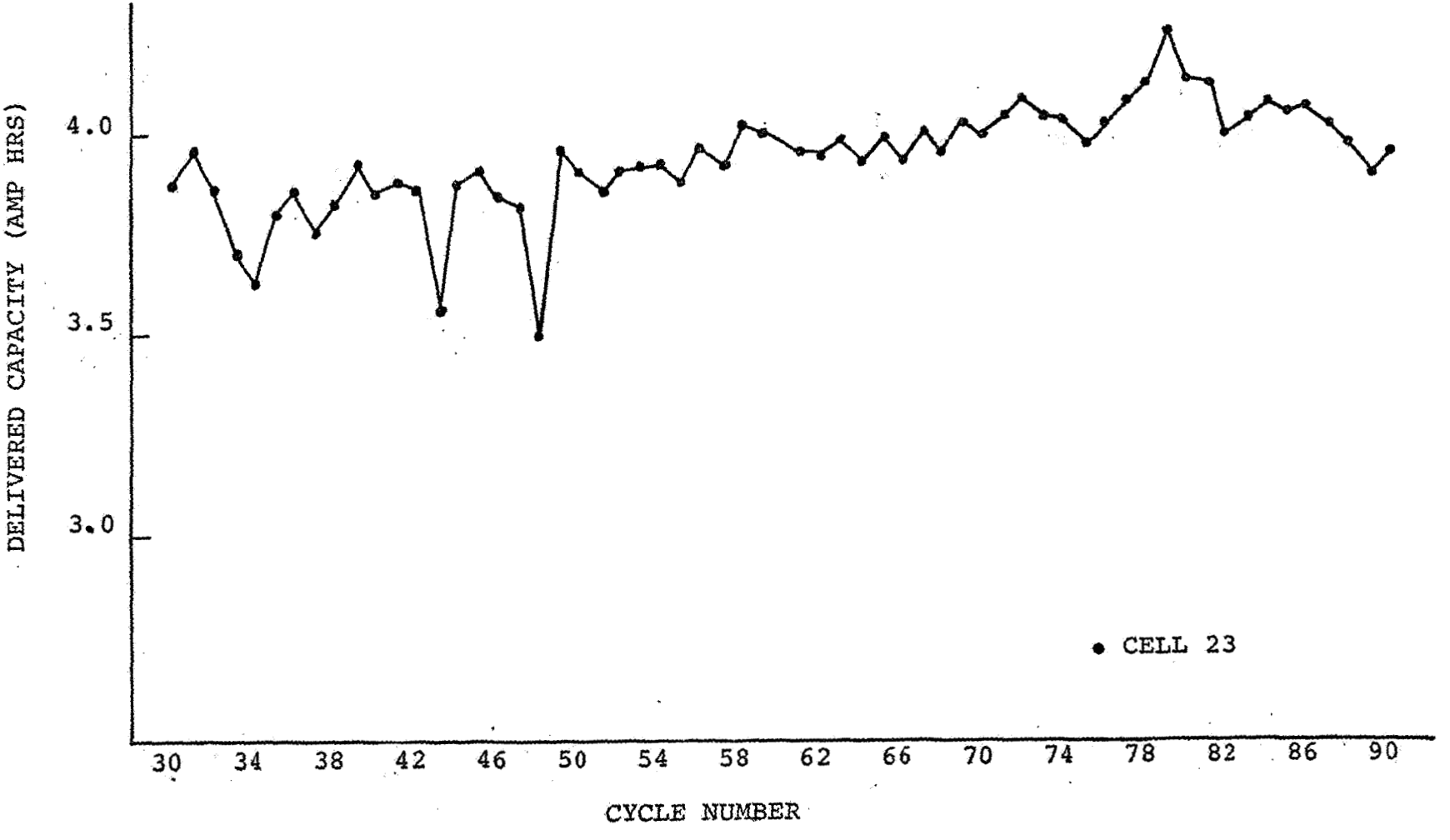


FIG. 5

AMPERE CAPACITY OF 17 PLATE FACTORIAL CELLS VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR

34% KOH, 80% PORE FILL

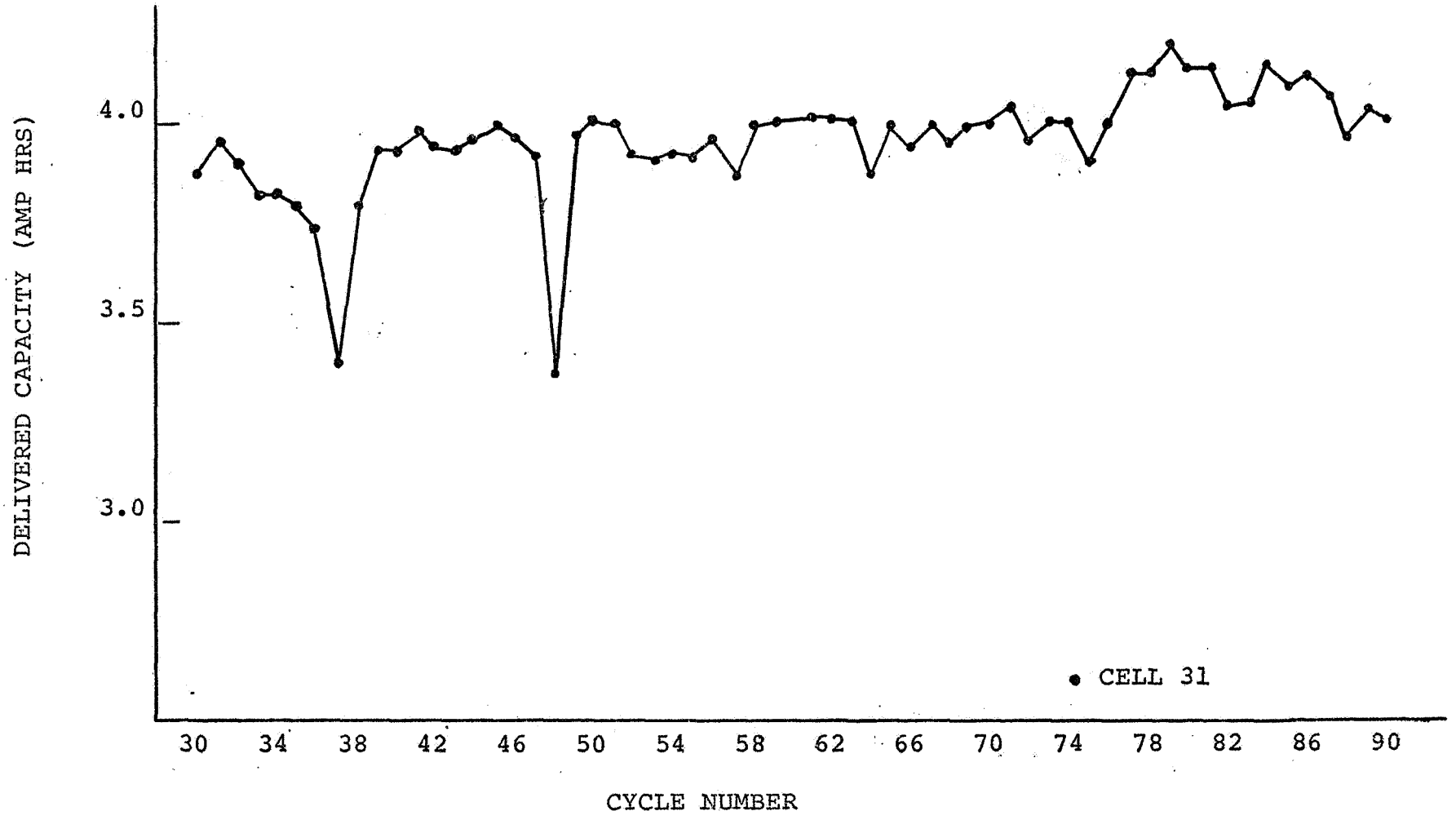


FIG. 6

END-OF-CHARGE VOLTAGE OF 17 PLATE FACTORIAL CELLS VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR

30% KOH, 70% PORE FILL

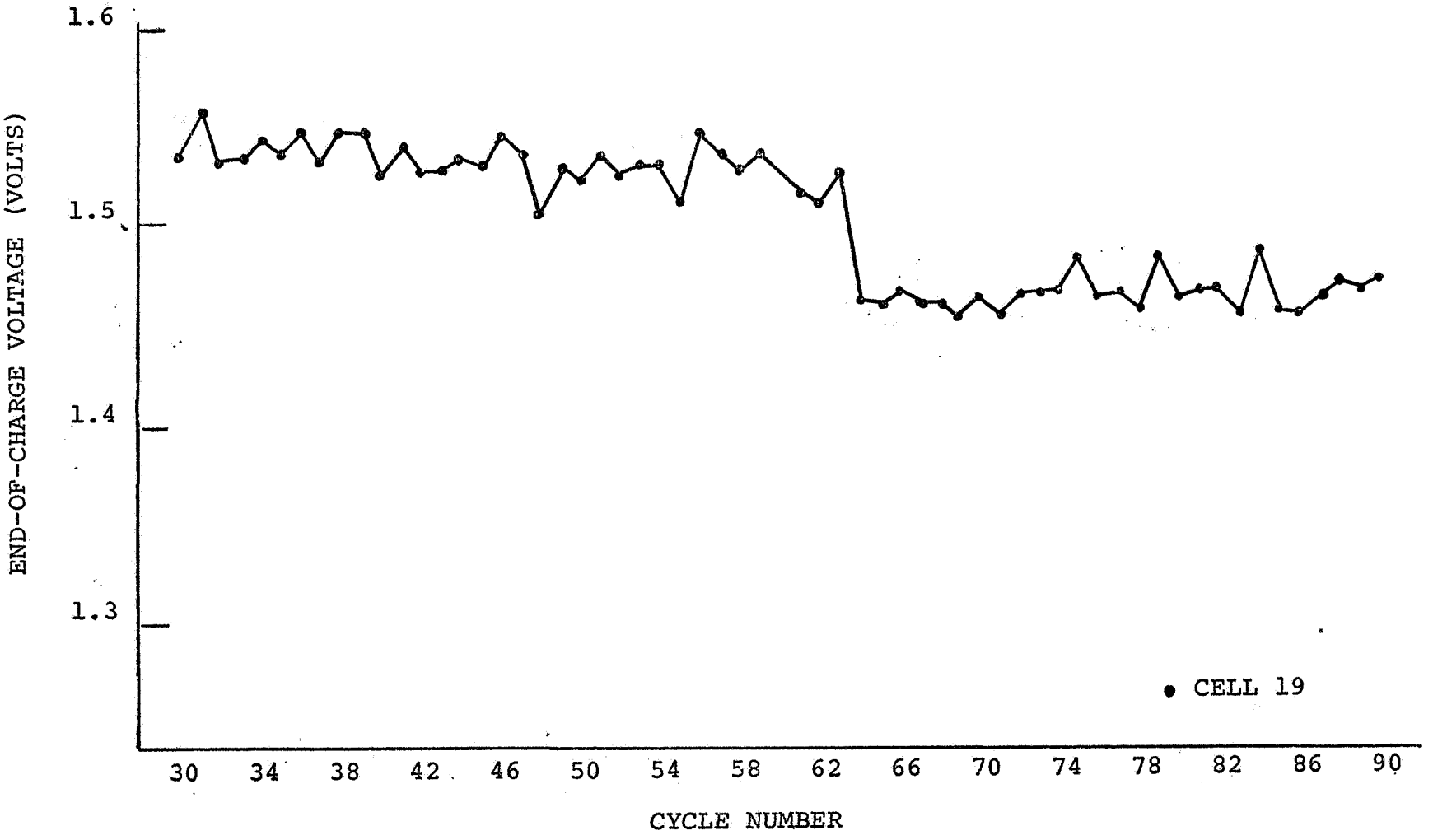


FIG. 7

END-OF-CHARGE VOLTAGE OF 17 PLATE FACTORIAL CELLS VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT 2140 SEPARATOR

30% KOH, 70% PORE FILL

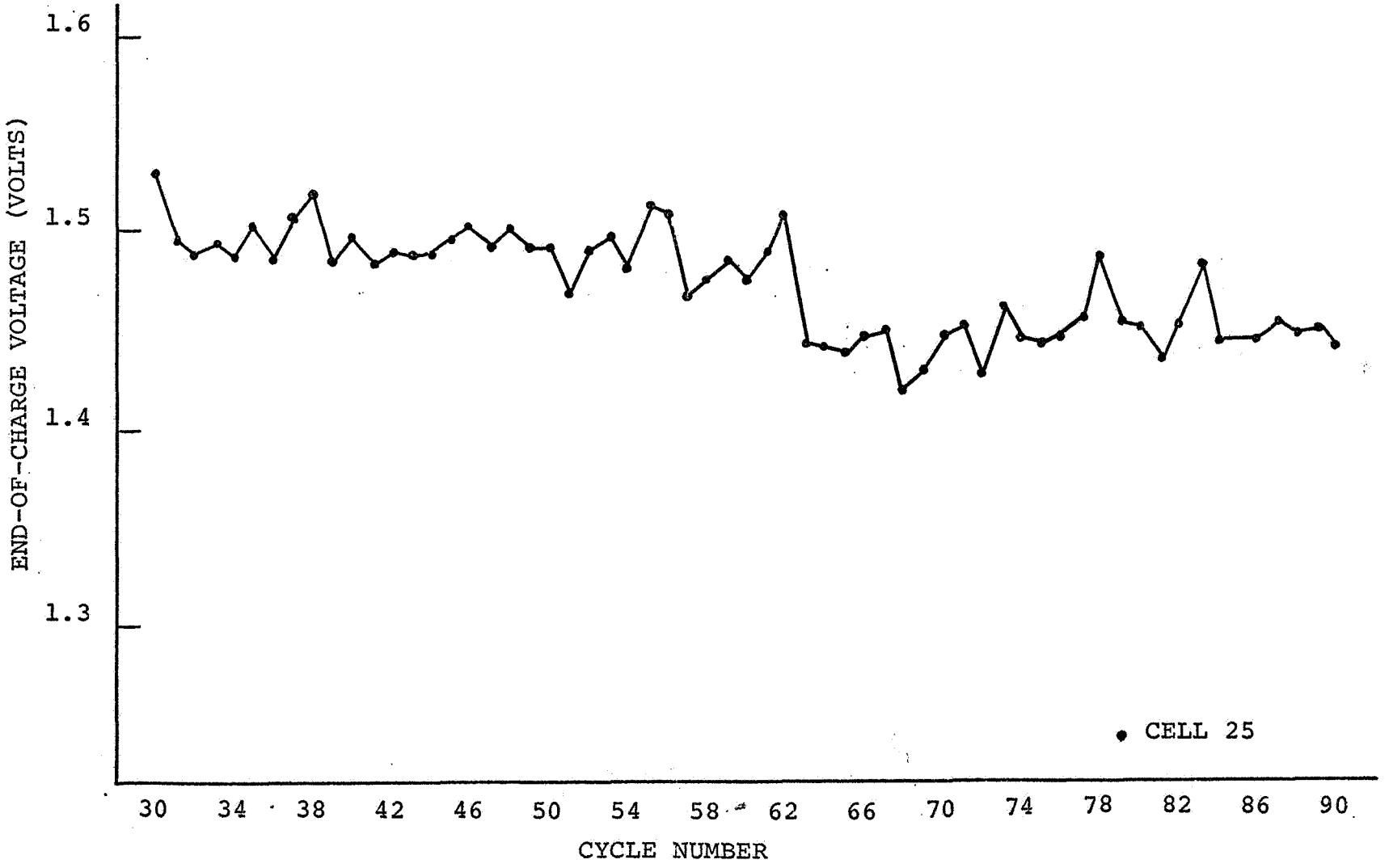


FIG. 8

END-OF-CHARGE VOLTAGE OF 17 PLATE FACTORIAL CELLS VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR

30% KOH, 80% PORE FILL

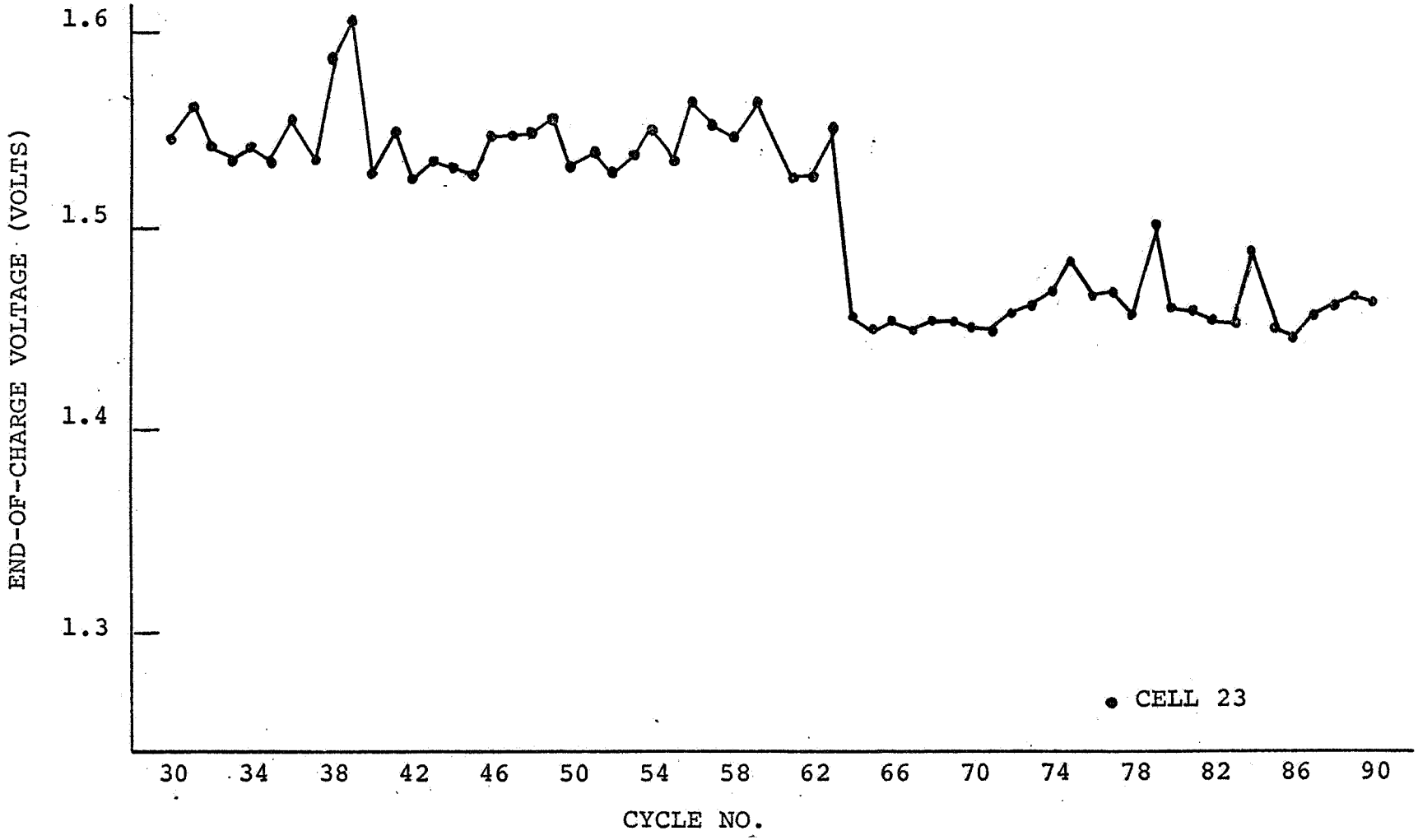


Fig. 9

END-OF-CHARGE VOLTAGE OF 17 PLATE FACTORIAL CELLS VS. CYCLE NUMBER
POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR
34% KOH, 80% PORE FILL

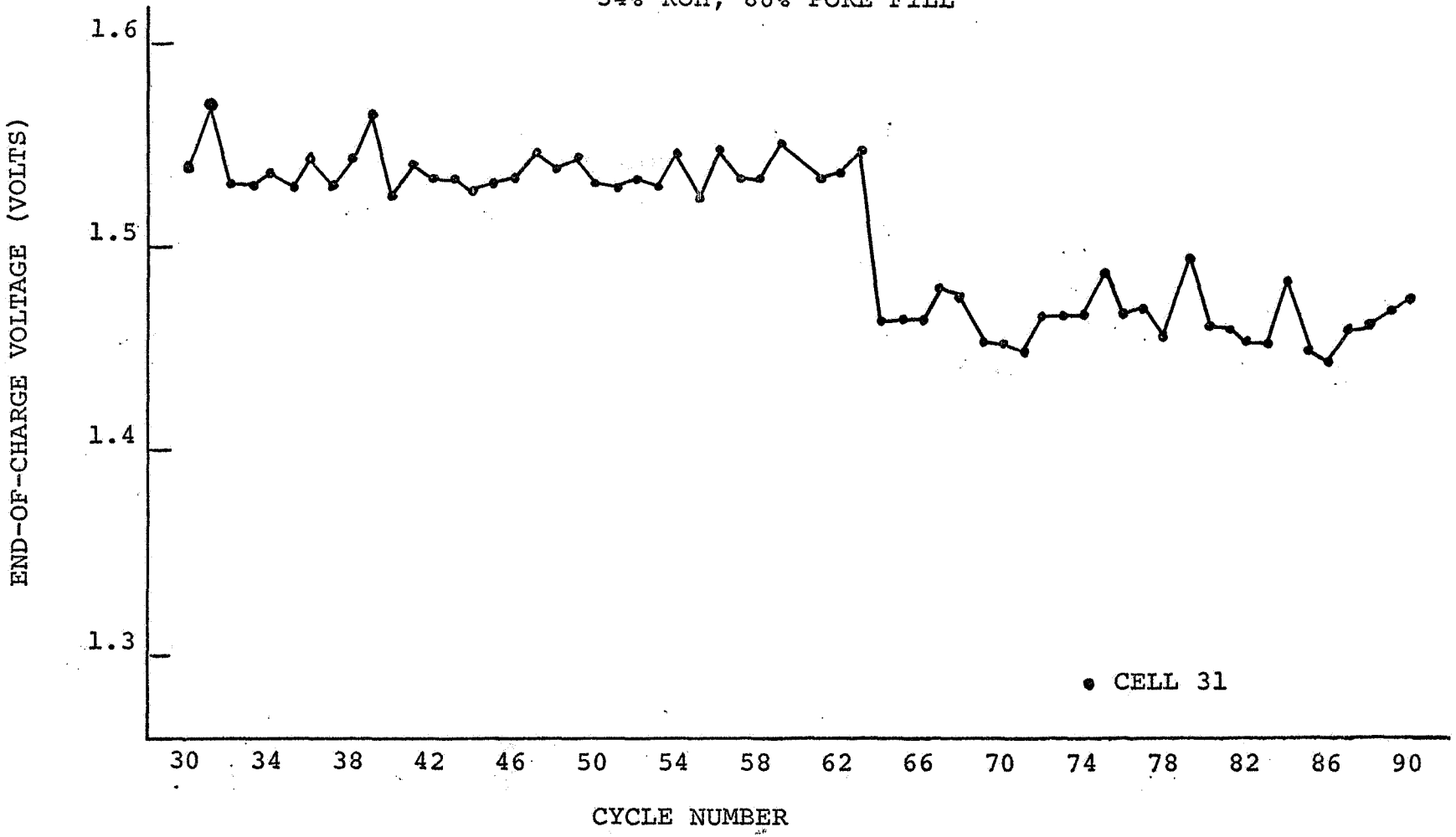


FIG. 10

END-OF-CHARGE RESISTANCE OF 17 PLATE FACTORIAL CELL VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR

30% KOH, 70% PORE FILL

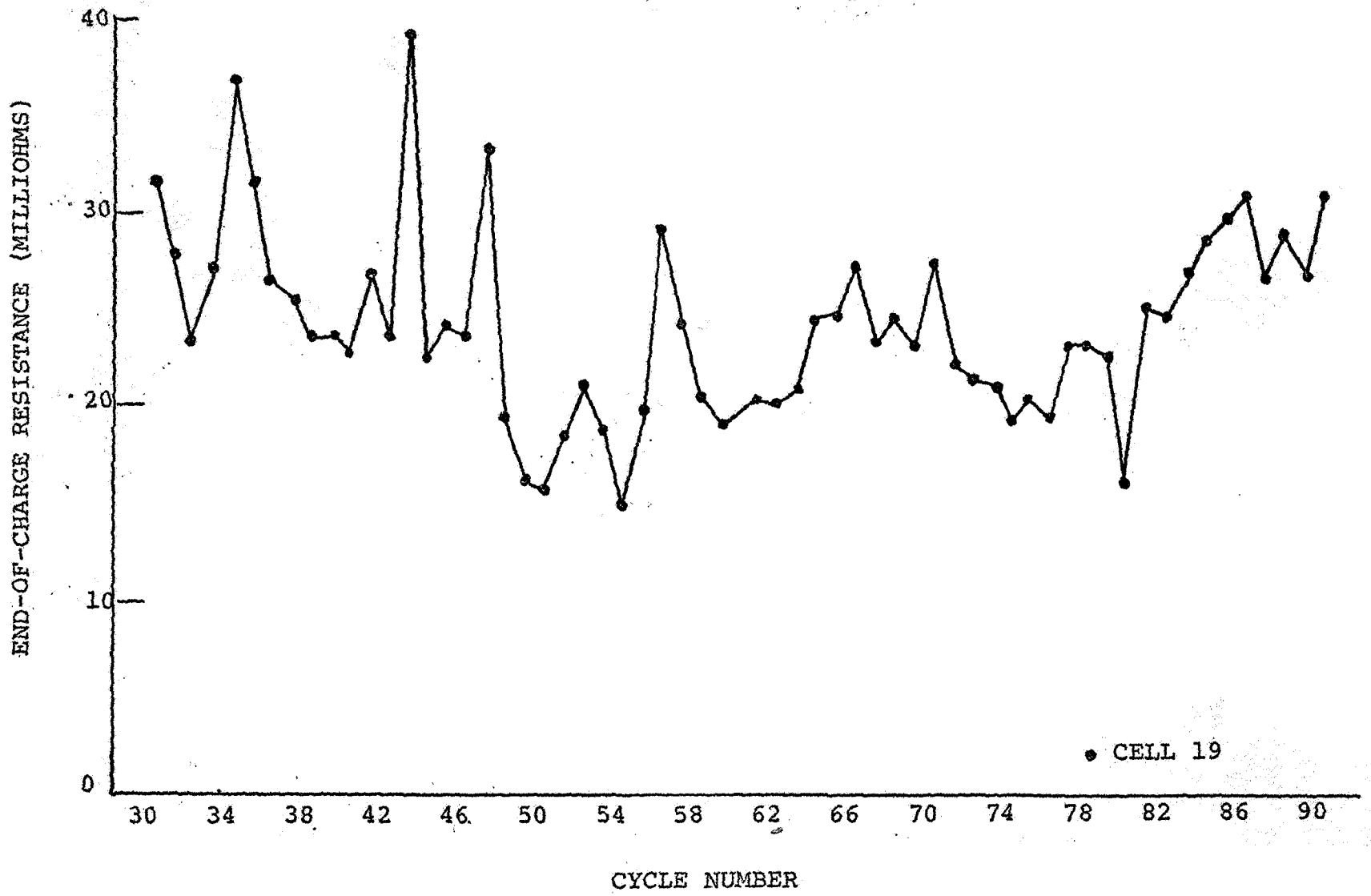


FIG. 11

END-OF-CHARGE RESISTANCE OF 17 PLATE FACTORIAL CELL VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR

34% KOH, 70% PORE FILL

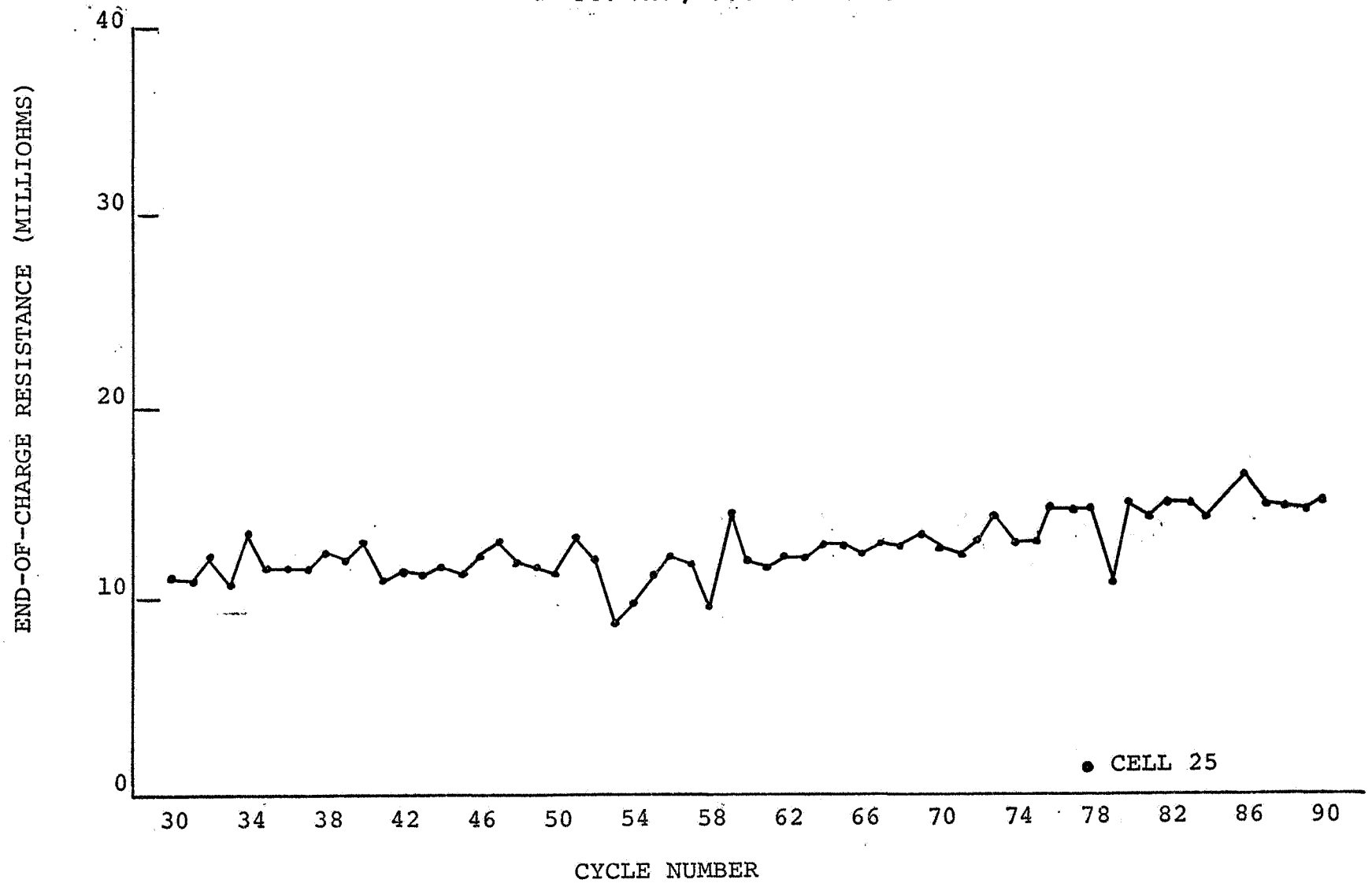


FIG. 12

END-OF-CHARGE RESISTANCE OF 17 PLATE FACTORIAL CELL VS. CYCLE NUMBER
POST STERILIZATION
CELL DESIGN: TYPE FT 2140 SEPARATOR

30% KOH, 80% PORE FILL

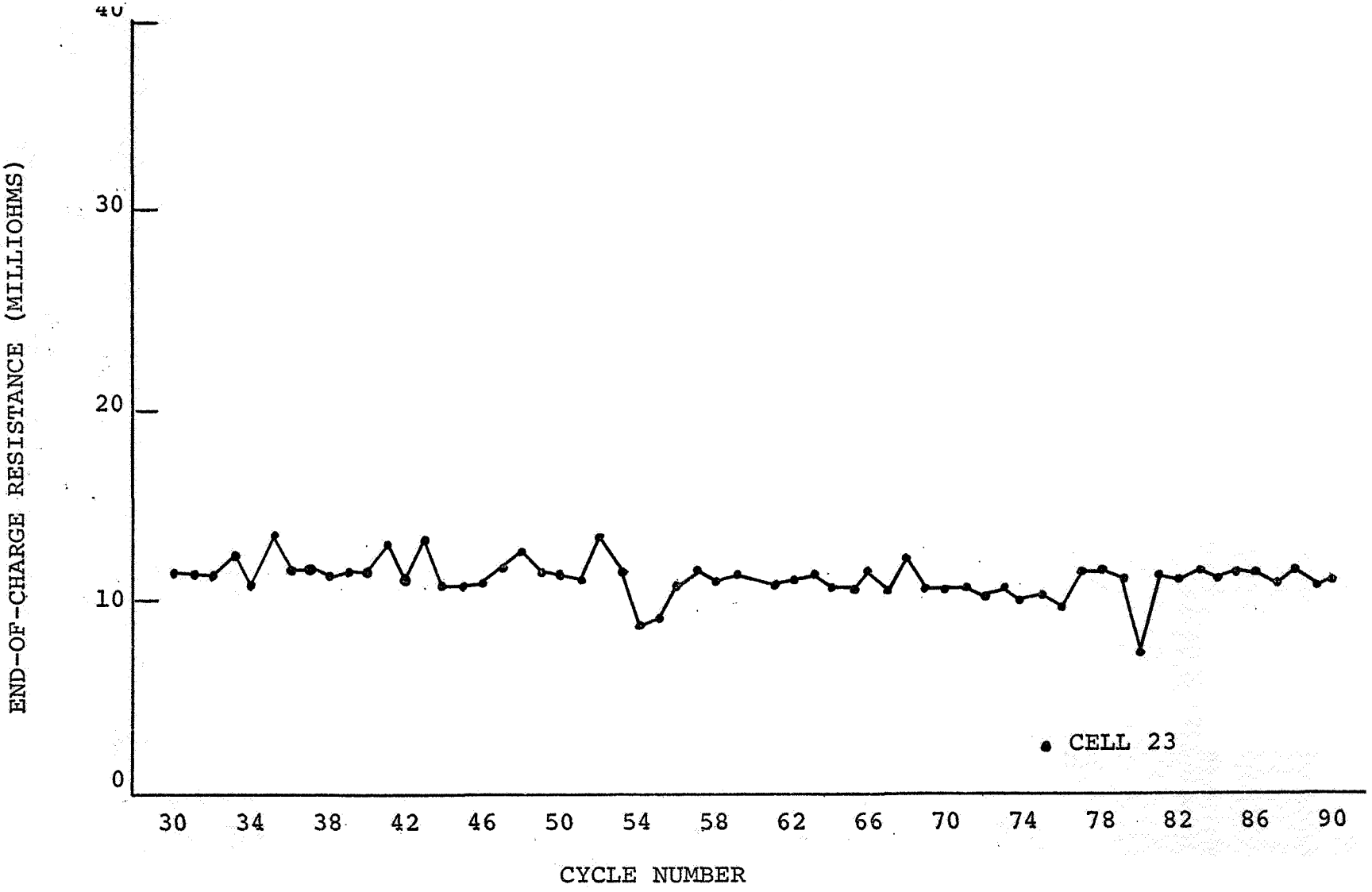


FIG. 13

END-OF-CHARGE RESISTANCE OF 17 PLATE FACTORIAL CELL VS. CYCLE NUMBER

POST STERILIZATION

CELL DESIGN: TYPE FT2140 SEPARATOR

34% KOH, 80% PORE FILL

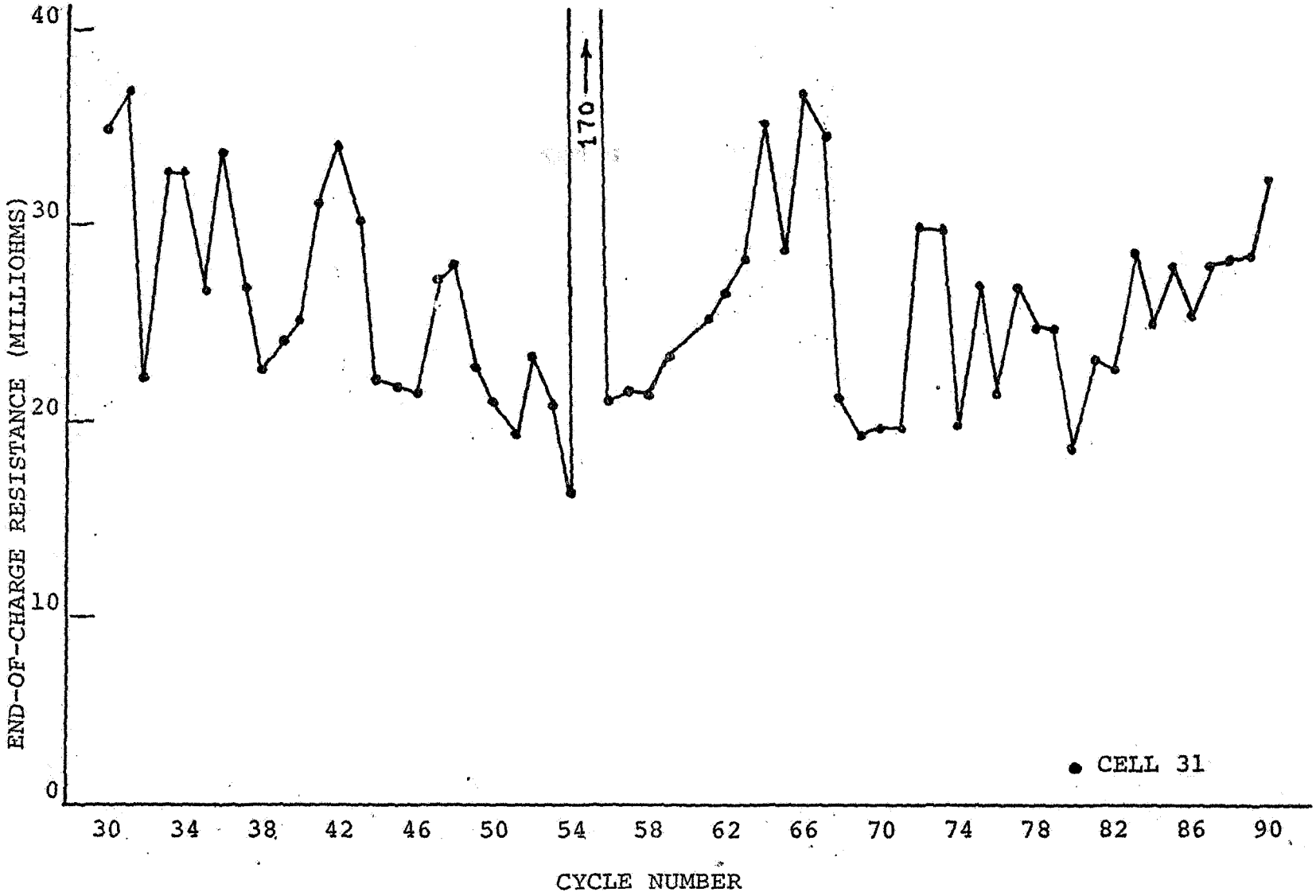
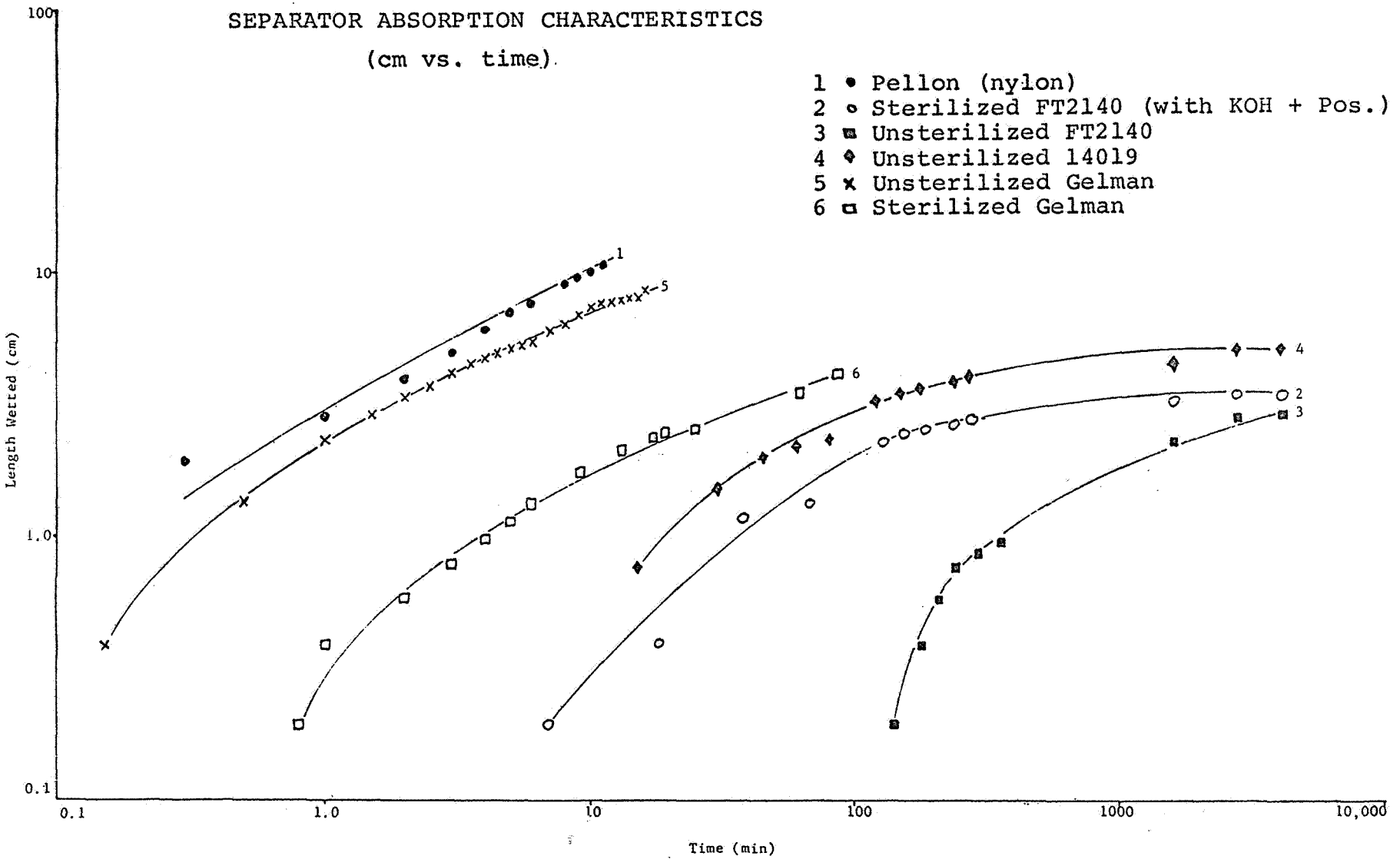


FIGURE 14


SEPARATOR ABSORPTION CHARACTERISTICS
(cm vs. time)
1 • Pellon (nylon)
2 ○ Sterilized FT2140 (with KOH + Pos.)
3 ■ Unsterilized FT2140
4 ♦ Unsterilized 14019
5 × Unsterilized Gelman
6 □ Sterilized Gelman
Length Wetted (cm)
100
10
1.0
0.1
0.1
1.0
10
100
1000
10,000
Time (min)

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